FORM PTO-1390 (Modified) (REV 11-2000) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES	220983US0PCT

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

10/089109

INTERNATIONAL APPLICATION NO. PCT/JP00/06959	INTERNATIONAL FILING DATE 05 OCTOBER 2000	PRIORITY DATE CLAIMED 08 OCTOBER 1999 (EARLIEST)

TITLE OF INVENTION

LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY CELL EMPLOYING IT, AND LITHIUM SECONDARY CELL

APPLICANT(S) FOR DO/EO/US

Manabu SUHARA, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
   - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
   - b. ☒ has been communicated by the International Bureau.
   - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   - a. ☒ is attached hereto.
   - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
   - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
   - b. ☐ have been communicated by the International Bureau.
   - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail.
23. ☒ Other items or information:

   Notice of Priority / PCT/IB/304 / PCT/IB/308
   PTO-1449

PCTUS1/REV03

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR **10/089109**	INTERNATIONAL APPLICATION NO. **PCT/JP00/06959**	ATTORNEY'S DOCKET NUMBER **220983US0PCT**

	CALCULATIONS	PTO USE ONLY

24. The following fees are submitted:.

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

☐ Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO $1040.00

☒ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO $890.00

☐ International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO $740.00

☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) $710.00

☐ International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) $100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =	$890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).	$0.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	11 - 20 =	0	x $18.00	$0.00	
Independent claims	1 - 3 =	0	x $84.00	$0.00	
Multiple Dependent Claims (check if applicable).			☐	$0.00	

TOTAL OF ABOVE CALCULATIONS =	$890.00	
☐ Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.	$0.00	
SUBTOTAL =	$890.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492 (f)). +	$0.00	
TOTAL NATIONAL FEE =	$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). ☒	$40.00	
TOTAL FEES ENCLOSED =	$930.00	

	Amount to be: refunded	$
	charged	$

a. ☒ A check in the amount of _____$930.00_____ to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. _____15-0030_____ A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

[barcode] **22850**

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SIGNATURE _Surinder Sachar_

NAME **Norman F. Oblon**

REGISTRATION NUMBER **24,618**

DATE _March 26 2002_

220983US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF	:
MANABU SUHARA ET AL	: ATTN: APPLICATION DIVISION
SERIAL NO: NEW U.S. PCT APPLN (Based on PCT/JP00/06959)	:
FILED: HEREWITH	:

FOR: LITHIUM-COBALT COMPOSITE
OXIDE, PROCESS FOR ITS
PRODUCTION,
POSITIVE ELECTRODE FOR
LITHIUM SECONDARY CELL
EMPLOYING IT, AND
LITHIUM SECONDARY CELL

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as

follows.

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment

to read as follows:

4. (Amended) The hexagonal lithium-cobalt composite oxide for a lithium secondary

cell according to Claim 1, wherein the packing press density of the hexagonal lithium-cobalt

composite oxide is from 2.90 to 3.35 g/cm^3.

5. (Amended) A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20 μm and a specific surface area of from 2 to 200 m^2/g, a lithium carbonate powder having an average particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g, and a powder of an oxide of metal element M having an average particle size of at most 10 μm and a specific surface area of from 1 to 100 m^2/g, and firing the mixture at a temperature of from 850 to 1,000°C in an oxygen-containing atmosphere.

7. (Amended) A positive electrode for a lithium secondary cell, which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1, as an active material.

9. (Amended) The positive electrode for a lithium secondary cell according to Claim 7, wherein the current collector is aluminum or stainless steel.
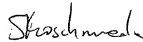
10. (Amended) A lithium secondary cell employing a positive electrode which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1, as an active material.

REMARKS

Claims 1-11 are active in the present application. Claims 4, 5, 7, 9 and 10 have been amended to remove multiple dependencies. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

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Marked-Up Copy
Serial No:

Amendment Filed on:
3-26-2002

IN THE CLAIMS

--4. (Amended) The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, [2 or 3,] wherein the packing press density of the hexagonal lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm^3.

5. (Amended) A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in [any one of Claims 1 to 4] Claim 1, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20 μm and a specific surface area of from 2 to 200 m^2/g, a lithium carbonate powder having an average particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g, and a powder of an oxide of metal element M having an average particle size of at most 10 μm and a specific surface area of from 1 to 100 m^2/g, and firing the mixture at a temperature of from 850 to 1,000°C in an oxygen-containing atmosphere.

7. (Amended) A positive electrode for a lithium secondary cell, which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in [any one of Claims 1 to 4] Claim 1, as an active material.

9. (Amended) The positive electrode for a lithium secondary cell according to Claim 7 [or 8], wherein the current collector is aluminum or stainless steel.

10. (Amended) A lithium secondary cell employing a positive electrode which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in [any one of Claims 1 to 4] Claim 1, as an active material.--

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DESCRIPTION

LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS

PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY CELL

EMPLOYING IT, AND LITHIUM SECONDARY CELL

5 TECHNICAL FIELD

The present invention relates to a lithium-cobalt

composite oxide for a lithium secondary cell, a process

for its production, a positive electrode for a lithium

secondary cell employing it, and a lithium secondary

10 cell.

BACKGROUND ART

In recent years, along with the progress in portable

or codeless equipments, a demand is mounting for a non-

aqueous electrolyte secondary cell which is small in size

15 and light in weight and has a high energy density. As an

active material for a non-aqueous electrolyte secondary

cell, a composite oxide of lithium and a transition

metal, such as $LiCoO_2$, $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$, $LiMn_2O_4$ or

$LiMnO_2$, has been known. Especially, a lithium secondary

20 cell employing a lithium-cobalt composite oxide ($LiCoO_2$)

as a positive electrode active material and employing a

lithium alloy or a carbon such as graphite or carbon

fiber as a negative electrode, provides a high voltage at

a level of 4 V and is widely used as a cell having a high

25 energy density.

However, a conventional lithium secondary cell has

had a problem of deterioration of the cycle

characteristics such that the cell discharge capacity gradually decreases as a charge/discharge cycle is repeated, or a problem that the safety is insufficient. Further, higher densification is required with respect to

5   the volume capacity density.

In order to improve such cell properties, JP-A-10-1316 proposes to use as an active material $LiCoO_2$ which is obtained by dispersing in an aqueous lithium hydroxide solution e.g. cobalt hydroxide or cobalt oxyhydroxide

10 wherein the valence of cobalt is trivalent, followed by heat treatment, for the purpose of improving the cycle characteristics, etc., of a lithium secondary cell.

Further, JP-A-10-279315 and JP-A-11-49519 propose to obtain a lithium secondary cell having a high capacity

15 and good cycle characteristics by using as an active material $LiCoO_2$ which is obtained by mixing e.g. dicobalt trioxide (Co_3O_2) or cobalt oxyhydroxide wherein the valence of cobalt is trivalent, with e.g. lithium oxide and firing such a mixture at a temperature of from 250 to

20 1,000°C.

Further, JP-A-10-312805 proposes to improve the cycle characteristics of a lithium secondary cell by using as a positive electrode active material $LiCoO_2$ of a hexagonal system having a crystallite diameter of from 45

25 to 100 nm in a (110) direction of the crystallite, wherein the length of c axis of lattice constant is at most 14.051 Å.

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Further, JP-A-7-32017 proposes to use as a positive electrode active material LiCoO$_2$ having from 5 to 35% of Co atoms replaced with W, Mn, Ta, Ti or Nb, for improvement of the cycle characteristics of a lithium

5   secondary cell. Further, JP-A-6-64928 proposes to improve the self-discharge characteristics of a lithium secondary cell by using as a positive electrode active material a Ti-containing lithium-cobalt composite oxide prepared by a synthesis employing a molten salt.

10   However, with respect to a lithium secondary cell using as a positive electrode active material a lithium-cobalt composite oxide, no product has been known which fully satisfies all of requirements for cycle characteristics, the initial weight capacity density, the

15   stability and the low temperature operation efficiency, and for a production method for efficient mass production.

It is an object of the present invention to provide a lithium-cobalt composite oxide for a lithium secondary

20   cell which has a large electric capacity and good discharge characteristics at low temperatures, is excellent in the charge/discharge cycle durability, and has an initial weight capacity density, a volume capacity density and high safety, a process for its production, a

25   positive electrode for a lithium secondary cell employing it, and such a cell.

DISCLOSURE OF THE INVENTION

The present inventors have found that when a lithium-cobalt composite oxide having a specific composition and crystal structure, is used as a positive

5   electrode for a lithium secondary cell, the cell properties will be excellent, and particularly, a lithium-cobalt composite oxide obtained by a specific production process is excellent in the productivity, and a lithium secondary cell wherein such a composite oxide

10   is used as a positive electrode active material, is especially excellent in cycle characteristics and is also excellent in safety and low temperature operation efficiency.

The present invention provides a hexagonal lithium-

15   cobalt composite oxide for a lithium secondary cell, which is represented by the formula $LiCo_{1-x}M_xO_2$, wherein x is $0 \leqq x \leqq 0.02$ and M is at least one member selected from the group consisting of Ta, Ti, Nb, Zr and Hf, and which has a half-width of the diffraction peak for (110) face

20   at $2\theta = 66.5 \pm 1°$, of from 0.070 to 0.180°, as measured by the X-ray diffraction using CuK_α as a ray source.

Further, the present invention provides a positive electrode for a lithium secondary cell, which contains the above hexagonal lithium-cobalt composite oxide for a

25   lithium secondary cell, as an active material.

In the formula of the above lithium-cobalt composite oxide, if x is larger than 0.02, the initial electric

capacity decreases, such being undesirable. Further,
with a view to improvement of safety and production
efficiency, x is preferably 0. Further, from the effects
for improvement of cycle durability and low temperature

5 operation efficiency, x is preferably $0.0005 \leqq x \leqq 0.02$,
particularly preferably $0.001 \leqq x \leqq 0.01$, further
preferably $0.002 \leqq x \leqq 0.007$.

The half-width of the diffraction peak for (110)
face at $2\theta = 66.5 \pm 1°$, as measured by the X-ray diffraction

10 using CuK_α as a ray source, of the above lithium-cobalt
composite oxide, reflects the crystallite diameter in a
certain specific direction of the lithium-cobalt
composite oxide, and a relation has been found such that
the larger the half width of the peak, the smaller the

15 crystallite diameter. In the present invention, the
half-width of the peak means the width of the peak at 1/2
of the height of the peak.

The half-width of the diffraction peak for (110)
face of the lithium-cobalt composite oxide of the present

20 invention is from 0.070 to 0.180°. If such a half-width
is less than 0.070°, the charge/discharge cycle
durability, initial electric capacity, average discharge
voltage or safety of the cell employing it as a positive
electrode active material, tends to deteriorate, such

25 being undesirable. If such a half-width exceeds 0.180°,
the initial electric capacity and safety of the cell tend
to be low, such being undesirable. In a case where x is

at least 0.005, a particularly preferred range is from
0.100 to 0.165°. In a case where x is 0, from 0.070 to
0.110° is preferred, and a particularly preferred range
is from 0.080 to 0.110°.

5   Further, the present invention provides a process
for producing a hexagonal lithium-cobalt composite oxide
for a lithium secondary cell, which comprises dry
blending a cobalt oxyhydroxide powder having an average
particle size of from 1 to 20 μm and a specific surface

10   area of from 2 to 200 m^2/g, a lithium carbonate powder
having an average particle size of from 1 to 50 μm and a
specific surface area of from 0.1 to 10 m^2/g, and a
powder of an oxide of metal element M having an average
particle size of at most 10 μm and a specific surface

15   area of from 1 to 200 m^2/g, which may be added as the
case requires, followed by firing from 850 to 1,000°C in
an oxygen-containing atmosphere, preferably from 4 to 30
hours.

        In the present invention, the average particle size

20   means a weight average particle diameter. In the present
invention, the average particle size is a particle size
at a point where the cumulative curve of mass becomes 50%
in the cumulative curve for the total mass of 100%
prepared by obtaining the particle size distribution

25   based on mass. This may be referred to also as a mass
base cumulative 50% diameter (for example, Chemical
Engineering Handbook "Fifth Edition" (compiled by

Chemical Engineering Association) p 220-221, Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd. Edition, vol. 21, 106-113 (Wiley-Interscience). The measurement of the particle size is carried out by thoroughly dispersing in

5 a medium such as water by means of e.g. ultrasonic treatment and measuring the particle size distribution (for example, by using Microtruck HRAX-100, manufactured by Nikkiso co., Ltd.).

For the process of the present invention, it is

10 preferred to use the above-described specific cobalt oxyhydroxide as a cobalt material. If the average particle size of the cobalt oxyhydroxide is less than 1 μm, the safety of the cell tends to decrease, or the packing density of the electrode layer tends to decrease,

15 whereby the electrical capacity per volume tends to decrease, such being undesirable. Further, if the average particle size of the cobalt oxyhydroxide exceeds 20 μm, the discharge characteristics of the cell at a large current tend to decrease, such being undesirable.

20 A preferred average particle size of the cobalt oxyhydroxide is from 4 to 15 μm.

The above-described cobalt oxyhydroxide may sometimes be produced in a hydrous state. In such a case, the specific surface area can hardly be measured.

25 Accordingly, in the present invention, the specific surface area of hydrous cobalt oxyhydroxide means the specific surface area with respect to a powder obtained

by drying the hydrate of cobalt oxyhydroxide at 120°C for
16 hours for dehydration. Further, when hydrous cobalt
oxyhydroxide is to be used, it is preferred to use a
powder after drying it. For example, it is preferred to
5   employ it after drying at 120°C for 16 hours. In the
present invention, if the specific surface area of the
cobalt oxyhydroxide is less than 2 m^2/g, the discharge
capacity at a large current tends to decrease, such being
undesirable. Further, if the specific surface area of
10   the cobalt oxyhydroxide exceeds 200 m^2/g, the packing
density of the positive electrode layer tends to
decrease, whereby the electric capacity per volume tends
to decrease, such being undesirable. A preferred
specific surface area of the cobalt oxyhydroxide is from
15   20 to 100 m^2/g.

     For the process of the present invention, it is
preferred to use lithium carbonate having a specific
nature, as a lithium material. If the average particle
size of the lithium carbonate is less than 1 μm, the bulk
20   density of the powder tends to decrease, and the
productivity in mass production tends to decrease, such
being undesirable. Further, if the average particle size
of the lithium carbonate exceeds 100 μm, the initial
electric capacity tends to decrease, such being
25   undesirable. A particularly preferred average particle
size of the lithium carbonate is from 5 to 30 μm. If the
specific surface area of the lithium carbonate is less

than $0.1 \ m^2/g$, the initial discharge capacity per unit
weight tends to decrease, such being undesirable.
Further, if the specific surface area of the lithium
carbonate exceeds $10 \ m^2/g$, the packing density of the
5   positive electrode layer tends to decrease, whereby the
electric capacity per volume tends to decrease, such
being undesirable. A particularly preferred specific
surface area of the lithium carbonate is from 0.3 to 3
m^2/g.

10   In the process for producing a lithium-cobalt
composite oxide of the present invention, in a case where
M is contained, it is preferred to use a metal oxide
having a specific nature as a metal oxide containing
element M, as a raw material. The metal oxide containing
15   element M may preferably be titanium oxide TiO_2 when M is
titanium (Ti). Titanium oxide includes an anatase type,
a rutile type, etc. It is particularly preferred to use
an anatase type, since the cell properties will be good.
When M is niobium (Nb), Nb_2O_3 may preferably be
20   mentioned. When M is tantalum (Ta), Ta_2O_5 may preferably
be mentioned. When M is zirconium (Zr), zirconium oxide
ZrO_2 may preferably be mentioned. When M is hafnium
(Hf), HfO_2 may preferably be mentioned.

    If the average particle size of the metal oxide
25   containing element M exceeds 10 μm, the distribution of
element M in the lithium-cobalt composite oxide particles
tends to be non-uniform, whereby the effects of adding

element M relating to the cell performance tend to decrease, such being undesirable. A preferred average particle size of the oxide of element M is at most 1 μm, particularly preferably at most 0.3 μm.

5   If the specific surface area of the metal oxide containing element M is less than 1 m^2/g, the reactivity tends to decrease, whereby the effects of adding element M relating to the cell performance tend to decrease, such being undesirable. On the other hand, if the specific

10   surface area of the metal oxide containing element M exceeds 100 m^2/g, element M tends to be uniformly incorporated into the crystal lattice, whereby the effects of adding element M relating to the cell performance tend to decrease, such being undesirable. A

15   preferred specific surface area of the oxide of element M is from 2 to 20 m^2/g.

     The lithium-cobalt composite oxide of the present invention is preferably obtained by preferably dry blending the cobalt oxyhydroxide powder, the lithium

20   carbonate powder and the oxide powder containing element M, followed by firing from 850 to 1,000°C preferably for from 4 to 30 hours in an oxygen-containing atmosphere. Wet blending is not preferred, since the productivity is low. If the firing temperature is lower than 850°C, the

25   charge/discharge cycle durability tends to be low, such being undesirable. On the other hand, if the firing temperature exceeds 1,000°C, the initial electric

capacity tends to decrease, such being undesirable.
Particularly preferred is from 870 to 960°C, and more
preferred is from 880 to 920°C. If the firing time is
less than 4 hours, the firing state tends to be non-

5   uniform during mass production, whereby fluctuation is
likely to result in the properties, such being
undesirable. If it exceeds 30 hours, the productivity
tends to decrease, such being undesirable. It is
particularly preferred to employ a firing time of from 8

10 to 20 hours.

   The firing of the above mixture is carried out
preferably in an oxygen stream. The oxygen concentration
in the stream is preferably from 10 to 100 volume%,
particularly preferably from 19 to 50 volume%. If the

15 oxygen concentration is low, the cell performance tends
to deteriorate, such being undesirable.

   A lithium secondary cell employing a positive
electrode containing as an active material the lithium-
cobalt composite oxide obtained by the process of the

20 present invention and having the specific value of the
half-width of the diffraction peak for (110) face, has a
higher low temperature operation efficiency than ever,
and is excellent in the charge/discharge cycle
durability, while maintaining the initial electric

25 capacity.

   Among the lithium-cobalt composite oxides of the
present invention, one wherein the packing press density

of the lithium-cobalt composite oxide is from 2.90 to
3.35 g/cm^3, is preferred, since the capacity density per
unit volume of the electrode layer of the positive
electrode, can be made high. In the present invention,
5   the packing press density means an apparent density of a
press-molded product when the lithium-cobalt composite
oxide powder is pressed under a load of 0.3 t/cm^2. If
the packing press density is less than 2.90 g/cm^3, the
density of the electrode layer of the positive electrode
10   tends to be low, whereby the capacity per volume tends to
be low, such being undesirable. If the packing press
density exceeds 3.35 g/cm^3, the capacity development at a
high current density of the cell tends to deteriorate,
such being undesirable. The packing press density of the
15   lithium-cobalt composite oxide is particularly preferably
from 3.05 to 3.25 g/cm^3.

In the lithium secondary cell of the present
invention, it is preferred that a dispersion made of a
kneaded product or a slurry comprising the powder of the
20   lithium-cobalt composite oxide of the present invention,
an electrically conductive material, a binder and a
solvent or dispersant for the binder, is coated on a
positive electrode current collector made of e.g. an
aluminum foil or a stainless steel foil, and then dried
25   to have it supported on the current collector to obtain a
positive electrode. As the electrically conductive
material, a carbon type conductive material such as

acetylene black, graphite or ketjenblack, is, for
example, preferably employed. As the binder,
polyvinylidene fluoride, polytetrafluoroethylene,
polyamide, carboxymethyl cellulose or an acrylic resin

5   may, for example, preferably be employed. As the
separator, a porous polyethylene film or a porous
polypropylene film may, for example, preferably be
employed.

In the lithium secondary cell of the present

10 invention, as the solvent for the electrolyte solution, a
carbonic ester is preferred. The carbonic ester may be
cyclic or chain. The cyclic carbonic ester may, for
example, be propylene carbonate or ethylene carbonate
(EC). The chain carbonic ester may, for example, be

15 dimethyl carbonate, diethyl carbonate (DEC), ethylmethyl
carbonate, methylpropyl carbonate or methylisopropyl
carbonate.

In the lithium secondary cell of the present
invention, the above carbonic esters may be used alone or

20 in combination as a mixture of two or more of them.
Further, such an ester may be mixed with other solvent.
Further, depending upon the material for the negative
electrode active material, there may be a case where the
charge/discharge characteristics, cycle durability or

25 charge/discharge efficiency can be improved by a combined
use of a chain carbonic ester and a cyclic carbonic
ester.

Further, to such an organic solvent, a vinylidene fluoride/hexafluoropropylene copolymer (for example, Keiner, tradename, manufactured by Atochem Company) and vinylidene fluoride/perfluoropropyl vinyl ether copolymer

5   disclosed in JP-A-10-294131, may be added, and the following solute may be added to obtain a gel polymer electrolyte.

As the solute for the above electrolyte solution or polymer electrolyte, it is preferred to use at least one

10   member of lithium salts containing e.g. ClO_4-, CF_3SO_3-, BF_4-, PF_6-, AsF_6-, SbF_6-, CF_3CO_2- or $(CF_3SO_2)_2N-$ as an anion. For the above electrolyte solution or polymer electrolyte, it is preferred to add the electrolyte made of a lithium salt to the above solvent or solvent-

15   containing polymer at a concentration of from 0.2 to 2.0 mol/ℓ. If the concentration departs from this range, the ion conductivity tends to decrease, and the electrical conductivity of the electrolyte tends to decrease. The concentration is more preferably adjusted to be from 0.5

20   to 1.5 mol/ℓ.

In the lithium secondary cell employing a positive electrode active material of the present invention, as the negative electrode active material, a material capable of absorbing and desorbing lithium ions, is

25   employed. The material for such a negative electrode active material is not particularly limited, but, it may, for example, be a lithium metal, a lithium alloy, a

carbon material, an oxide composed mainly of a metal of

Group 14 or 15 of the Periodic Table, a carbon compound,

a silicon carbide compound, a silicon oxide compound,

titanium sulfide or a boron carbide compound. As the

5 carbon material, one obtained by thermally decomposing an

organic material by various thermal decomposition

conditions, or artificial graphite, natural graphite,

soil graphite, expanded graphite or scaly graphite, may,

for example, be used. Further, as the oxide, a compound

10 composed mainly of tin oxide, may be used. As the

negative electrode current collector, a copper foil or a

nickel foil may, for example, be used.

The negative electrode in the present invention is

obtained preferably by kneading the above-mentioned

15 negative electrode active material with an organic

solvent in the same manner as in the case of the above

positive electrode, to obtain a slurry, and coating the

slurry on a metal foil current collector, followed by

drying and pressing. There is no particular restriction

20 as to the shape of the lithium secondary cell of the

present invention. A sheet shape (so-called film shape),

folded-shape, wounded bottomed cylindrical shape or a

button shape, may suitably be selected depending upon the

particular application.

25 Now, the present invention will be described in

further detail with reference to Examples, but it should

be understood that the present invention is by no means

restricted to such Examples. The following Examples 1 to

14 are Examples of the present invention, and Examples 15

and 16 are Comparative Examples.

EXAMPLE 1

5   A cobalt oxyhydroxide powder having an average

particle size of 10 μm and a specific surface area of 66

m^2/g, a lithium carbonate powder having an average

particle size of 15 μm and a specific surface area of 1.2

m^2/g and an anatase-type titanium dioxide powder having

10   an average particle size of 0.22 μm and a specific

surface area of 9 m^2/g, were mixed. The mixing ratio was

such that the composition would be $LiCo_{0.998}Ti_{0.002}O_2$ after

firing. These three types of powders were dry-blended

and then fired at 910°C for 12 hours in an atmosphere

15   having the oxygen concentration adjusted to 28 volume% by

adding oxygen gas to air.

With respect to the powder after the firing (the

positive electrode active material powder), the X-ray

diffraction spectrum was obtained by using RINT 2100

20   model X-ray diffraction apparatus, manufactured by Rigaku

Corporation. By this powder X-ray diffraction using CuK_α

ray, a diffraction peak of a hexagonal system was

obtained. Further, the half-width of the diffraction

peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

25   0.121°.

This positive electrode active material powder was

pressed under 0.3 t/cm^2, and the packing press density

was determined from the volume and the weight and found
to be 3.20 g/cm^3. The LiCo$_{0.998}$Ti$_{0.002}$O$_2$ powder thus
obtained, acetylene black and a polytetrafluoroethylene
powder, were mixed in a weight ratio of 80/16/4 and
5   kneaded while adding toluene, followed by drying to
obtain a positive electrode plate having a thickness of
150 μm.

    And, two stainless steel simple closed cells were
assembled in an argon grove box, by using an aluminum
10 foil having a thickness of 20 μm as a positive electrode
current collector, using a porous polypropylene film
having a thickness of 25 μm as a separator, using a metal
lithium foil having a thickness of 500 μm as a negative
electrode, using a nickel foil of 20 μm as a negative
15 electrode current collector, and using 1M LiPF$_6$/EC+DEC
(1:1) as an electrolyte.

    With respect to these two cells, firstly, charging
was carried out to 4.3 V at a load current of 75 mA per g
of the electrode active material at 25°C, and discharging
20 was carried out to 2.5 V at an applied current of 75 mA
per g of the positive electrode active material, whereby
the initial discharge capacity was obtained. With
respect to one cell, the charge/discharge cycle test was
further carried out 40 times. Further, the other cell
25 was charged at 25°C and then cooled to −10°C. Then,
discharging was carried out to 2.5 V by a load current of
75 mA per g of the positive electrode active material,

whereby the initial discharge capacity at $-10°C$ was obtained, and the capacity development rate at $-10°C$ was obtained, on the basis that the initial electric capacity at 25°C was 100%.

5   The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.3%. Further, the capacity developing rate at $-10°C$ was 70%.

EXAMPLE 2

10   A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m^2/g, a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m^2/g and an niobium oxide Nb_2O_5 powder having an average particle size of 0.15 μm and a specific surface area of 5.3 m^2/g, were mixed. The mixing ratio was such that the composition would be $LiCo_{0.998}Nb_{0.002}O_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

     With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was 0.115°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.23 g/cm^3.

Two stainless steel simple closed cells were
5 assembled in the same manner as in Example 1 except that the above $LiCo_{0.998}Nb_{0.002}O_2$ powder was used instead of the $LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby
10 the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.0%. Further, the capacity developing rate at -10°C was 73%.

EXAMPLE 3
15 A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m^2/g, a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m^2/g and a tantalum oxide Ta_2O_5 powder having an average
20 particle size of 0.23 μm and a specific surface area of 9.8 m^2/g, were mixed. The mixing ratio was such that the composition would be $LiCo_{0.998}Ta_{0.002}O_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen
25 concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the

positive electrode active material powder), the
measurement was carried out in the same manner as in
Example 1, whereby the half-width of the diffraction peak
for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

5   0.115°.

The packing press density of this positive electrode
active material powder was determined in the same manner
as in Example 1, and found to be 3.19 g/cm^3.

Two stainless steel simple closed cells were

10   assembled in the same manner as in Example 1 except that
the above $LiCo_{0.998}Ta_{0.002}O_2$ powder was used instead of the
$LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

With respect to these two cells, the measurement was
carried out in the same manner as in Example 1, whereby

15   the initial discharge capacity at from 2.5 to 4.3 V at
25°C was 148 mAh/g, and the capacity retention after 40
charge/discharge cycles, was 96.1%. Further, the
capacity developing rate at -10°C was 75%.
EXAMPLE 4

20   A cobalt oxyhydroxide powder having an average
particle size of 8 μm and a specific surface area of 40
m^2/g, a lithium carbonate powder having an average
particle size of 22 μm and a specific surface area of
0.64 m^2/g and an anatase-type titanium dioxide powder

25   having an average particle size of 0.17 μm and a specific
surface area of 35 m^2/g, were mixed. The mixing ratio
was such that the composition would be $LiCo_{0.994}Ti_{0.006}O_2$

after firing. These three types of powders were dry-blended and then fired at 890°C for 15 hours in an atmosphere having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

5   With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

10   0.127°.

     The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.11 g/cm^3.

     Two stainless steel simple closed cells were

15   assembled in the same manner as in Example 1 except that the above $LiCo_{0.994}Ti_{0.006}O_2$ powder was used instead of the $LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

     With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby

20   the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.7%. Further, the capacity developing rate at −10°C was 72%.

EXAMPLE 5

25   A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m^2/g, a lithium carbonate powder having an average

particle size of 15 μm and a specific surface area of 1.2 m^2/g and a zirconium oxide (ZrO$_2$) powder having an average particle size of 8.1 μm and a specific surface area of 15 m^2/g, were mixed. The mixing ratio was such

5   that the composition would be LiCo$_{0.998}$Zr$_{0.002}$O$_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

10   With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

15   0.117°.

      The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.19 g/cm^3.

      Two stainless steel simple closed cells were

20   assembled in the same manner as in Example 1 except that the above LiCo$_{0.998}$Zr$_{0.002}$O$_2$ powder was used instead of the LiCo$_{0.998}$Ti$_{0.002}$O$_2$ powder in Example 1.

      With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby

25   the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.8%. Further, the

capacity developing rate at −10°C was 68%.

EXAMPLE 6

A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m²/g, a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m²/g and a hafnium oxide (HfO_2) powder having an average particle size of 0.4 μm and a specific surface area of 7.2 m²/g, were mixed. The mixing ratio was such that the composition would be $LiCo_{0.998}Hf_{0.002}O_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was 0.119°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.18 g/cm³.

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $LiCo_{0.998}Hf_{0.002}O_2$ powder was used instead of the $LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40

5 charge/discharge cycles, was 96.0%. Further, the capacity developing rate at −10°C was 70%.

EXAMPLE 7

A cobalt oxyhydroxide powder having an average particle size of 8 μm and a specific surface area of 40

10 m^2/g, a lithium carbonate powder having an average particle size of 22 μm and a specific surface area of 0.64 m^2/g and a zirconium oxide powder having an average particle size of 8.1 μm and a specific surface area of 16 m^2/g, were mixed. The mixing ratio was such that the

15 composition would be $LiCo_{0.994}Zr_{0.006}O_2$ after firing. These three types of powders were dry-blended and then fired at 890°C for 15 hours in an atmosphere having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

20 With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

25 0.128°.

The packing press density of this positive electrode active material powder was determined in the same manner

as in Example 1, and found to be 3.10 g/cm^3.

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above LiCo$_{0.994}$Zr$_{0.006}$O$_2$ powder was used instead of the

5 LiCo$_{0.998}$Ti$_{0.002}$O$_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40

10 charge/discharge cycles, was 95.7%. Further, the capacity developing rate at −10°C was 72%.

EXAMPLE 8

A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66

15 m^2/g, and a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m^2/g, were mixed. The mixing ratio was such that the composition would be LiCoO$_2$ after firing. These three types of powders were dry-blended and then fired at 910°C

20 for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the

25 measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

0.098°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.10 g/cm^3.

5   Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above LiCoO$_2$ powder was used instead of the LiCo$_{0.998}$Ti$_{0.002}$O$_2$ powder in Example 1.

With respect to these two cells, the measurement was 10   carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 94.8%. Further, the capacity developing rate at −10°C was 54%.

15   EXAMPLE 9

A cobalt oxyhydroxide powder having an average particle size of 15 μm and a specific surface area of 60 m^2/g, and a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 20   m^2/g, were mixed. The mixing ratio was such that the composition would be LiCoO$_2$ after firing. These two types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas 25   to air.

With respect to the powder after the firing (the positive electrode active material powder), the

measurement was carried out in the same manner as in
Example 1, whereby the half-width of the diffraction peak
for (110) face in the vicinity of $2\theta=66.5\pm1°$, was
0.091°.

5   The packing press density of this positive electrode
active material powder was determined in the same manner
as in Example 1, and found to be 3.18 g/cm^3.

Two stainless steel simple closed cells were
assembled in the same manner as in Example 1 except that
10   the above LiCoO$_2$ powder was used instead of the
LiCo$_{0.998}$Ti$_{0.002}$O$_2$ powder in Example 1.

With respect to one cell among them, charging was
carried out to 4.3 V by a load current of 75 mA per g of
the positive electrode active material at 25°C, and
15   discharging was carried out to 2.5 V at a load current of
75 mA per g of the positive electrode active material,
whereby the initial discharge capacity was obtained.
Further, with respect to this cell, the charge/discharge
cycle test was continuously carried out 30 times. As a
20   result, the initial discharge capacity at from 2.5 to 4.3
V at 25°C was 149 mAh/g, and the capacity retention after
30 charge/discharge cycles, was 96.3%.

Further, with respect to the other cell, charging
was carried out to 4.3 V at a constant current of 0.2 mA
25   per 1 cm^2 of the positive electrode area and disassembled
in the argon grove box, whereupon the positive electrode
sheet after charging was taken out. The positive

electrode sheet was washed and then punched out in a size
of 3 mm, and it was sealed together with EC in an
aluminum capsule. The temperature was raised at a rate
of 5°C/min by a scanning differential calorimeter,

5 whereby the heat generation initiation temperature was
measured. As a result, the heat generation initiation
temperature was 165°C.

EXAMPLE 10

A cobalt oxyhydroxide powder having an average

10 particle size of 8 μm and a specific surface area of 50
m^2/g, and a lithium carbonate powder having an average
particle size of 15 μm and a specific surface area of 1.2
m^2/g, were mixed. The mixing ratio was such that the
composition would be $LiCoO_2$ after firing. These two

15 types of powders were dry-blended and then fired at 910°C
for 12 hours in an atmosphere having the oxygen
concentration adjusted to 28 volume% by adding oxygen gas
to air.

With respect to the powder after the firing (the

20 positive electrode active material powder), the
measurement was carried out in the same manner as in
Example 1, whereby the half-width of the diffraction peak
for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was
0.095°.

25 The packing press density of this positive electrode
active material powder was determined in the same manner
as in Example 1, and found to be 3.01 g/cm^3.

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $LiCoO_2$ powder was used instead of the $LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

5   With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 9, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 30

10   charge/discharge cycles, was 97.0%.

Further, in the same manner as in Example 9, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation

15   temperature was 169°C.

EXAMPLE 11

A cobalt oxyhydroxide powder having an average particle size of 12 μm and a specific surface area of 66 m^2/g, and a lithium carbonate powder having an average

20   particle size of 28 μm and a specific surface area of 0.43 m^2/g, were mixed. The mixing ratio was such that the composition would be $LiCoO_2$ after firing. These two types of powders were dry-blended and then fired at 890°C for 18 hours in an atmosphere having the oxygen

25   concentration adjusted to 19 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the

positive electrode active material powder), the
measurement was carried out in the same manner as in
Example 1, whereby the half-width of the diffraction peak
for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was
0.083°.

The packing press density of this positive electrode
active material powder was determined in the same manner
as in Example 1, and found to be 3.12 g/cm^3.

Two stainless steel simple closed cells were
assembled in the same manner as in Example 1 except that
the above $LiCoO_2$ powder was used instead of the
$LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

With respect to one of them, the initial electric
capacity of the cell and the capacity after 30 cycles
were obtained in the same manner as in Example 9, whereby
the initial discharge capacity at from 2.5 to 4.3 V at
25°C was 148 mAh/g, and the capacity retention after 30
charge/discharge cycles, was 95.3%.

Further, in the same manner as in Example 9, with
respect to the other cell, the reactivity of the charged
positive electrode active material with the electrolyte
was determined, whereby the heat generation initiation
temperature was 173°C.

EXAMPLE 12

$LiCoO_2$ was synthesized in the same manner as in
Example 9 except that a cobalt oxide (Co_3O_4) powder
having an average particle size of 8 μm and a specific

surface area of 0.66 m^2/g was used instead of cobalt
oxyhydroxide.

With respect to the powder after the firing (the
positive electrode active material powder), the

5   measurement was carried out in the same manner as in
Example 9, whereby the half-width of the diffraction peak
for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was
0.133°.

The packing press density of this positive electrode

10   active material powder was determined in the same manner
as in Example 1, and found to be 2.75 g/cm^3.

Two stainless steel simple closed cells were
assembled in the same manner as in Example 1 except that
the above LiCoO$_2$ powder was used instead of the LiCoO$_2$

15   powder in Example 9.

With respect to one of them, the initial electric
capacity of the cell and the capacity after 30 cycles
were obtained in the same manner as in Example 9, whereby
the initial discharge capacity at from 2.5 to 4.3 V at

20   25°C was 148 mAh/g, and the capacity retention after 30
charge/discharge cycles, was 96.4%.

Further, in the same manner as in Example 9, with
respect to the other cell, the reactivity of the charged
positive electrode active material with the electrolyte

25   was determined, whereby the heat generation initiation
temperature was 155°C.

EXAMPLE 13

LiCoO$_2$ was synthesized in the same manner as in the
above Example 9 except that a cobalt oxyhydroxide powder
having an average particle size of 30 μm and a specific
5   surface area of 7 m^2/g was used instead of the cobalt
oxyhydroxide powder having an average particle size of 15
μm and a specific surface area of 60 m^2/g.

With respect to the powder after the firing (the
positive electrode active material powder), the
10 measurement was carried out in the same manner as in
Example 1, whereby the half-width of the diffraction peak
for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was
0.118°.

The packing press density of this positive electrode
15 active material powder was determined in the same manner
as in Example 1, and found to be 3.15 g/cm^3.

Two stainless steel simple closed cells were
assembled in the same manner as in Example 1 except that
the above LiCoO$_2$ powder was used instead of the LiCoO$_2$
20 powder in Example 9.

With respect to one of them, the initial electric
capacity of the cell and the capacity after 30 cycles
were obtained in the same manner as in Example 9, whereby
the initial discharge capacity at from 2.5 to 4.3 V at
25 25°C was 137 mAh/g, and the capacity retention after 30
charge/discharge cycles, was 92.3%.

Further, in the same manner as in Example 9, with

respect to the other cell, the reactivity of the charged

positive electrode active material with the electrolyte

was determined, whereby the heat generation initiation

temperature was 158°C.

5   EXAMPLE 14

$LiCoO_2$ was synthesized in the same manner as in the

above Example 9 except that the firing at a temperature

of 910°C for 12 hours in Example 9 was changed to the

firing at 780°C for 12 hours.

10   With respect to the powder after the firing (the

positive electrode active material powder), the

measurement was carried out in the same manner as in

Example 1, whereby the half-width of the diffraction peak

for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was

15   0.138°.

The packing press density of this positive electrode

active material powder was determined in the same manner

as in Example 1, and found to be 2.98 g/cm^3.

Two stainless steel simple closed cells were

20   assembled in the same manner as in Example 1 except that

the above $LiCoO_2$ powder was used instead of the $LiCoO_2$

powder in Example 9.

With respect to one of them, the initial electric

capacity of the cell and the capacity after 30 cycles

25   were obtained in the same manner as in Example 9, whereby

the initial discharge capacity at from 2.5 to 4.3 V at

25°C was 147 mAh/g, and the capacity retention after 30

charge/discharge cycles, was 96.5%.

Further, in the same manner as in Example 9, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte

5   was determined, whereby the heat generation initiation temperature was 156°C.

EXAMPLE 15

$LiCo_{0.95}Ti_{0.05}O_2$ was synthesized in the same manner as in Example 1 except that the mixing ratio of the cobalt

10 oxyhydroxide powder, the lithium carbonate powder and the anatase-type titanium dioxide powder was changed so that the composition would be $LiCo_{0.95}Ti_{0.05}O_2$ after firing.

With respect to the powder after the firing (the positive electrode active material powder), the

15 measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta=66.5\pm1°$, was 0.188°.

Two stainless steel simple closed cells were

20 assembled in the same manner as in Example 1 except that the above $LiCo_{0.95}Ti_{0.05}O_2$ powder was used instead of the $LiCo_{0.998}Ti_{0.002}O_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby

25 the initial electric capacity at from 2.5 to 4.3 V at 25°C was 141 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 93.6%. Further, the

capacity developing rate at -10°C was 68%.

EXAMPLE 16

$LiCo_{0.95}Zr_{0.05}O_2$ was synthesized in the same manner as in Example 5 except that the mixing ratio of the cobalt oxyhydroxide powder, the lithium carbonate powder and zirconium oxide was changed so that the composition would be $LiCo_{0.95}Zr_{0.05}O_2$ after firing.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 5, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1°$, was 0.183°.

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $LiCo_{0.95}Zr_{0.05}O_2$ powder was used instead of the $LiCo_{0.998}Zr_{0.002}O_2$ powder in Example 5.

With respect to these two cells, the measurement was carried out in the same manner as in Example 5, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 140 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 93.8%. Further, the capacity developing rate at -10°C was 68%.

INDUSTRIAL APPLICABILITY

According to the present invention, a hexagonal lithium cobalt composite oxide having excellent properties as a positive electrode active material for a

lithium secondary cell which has a large electric capacity, good low temperature discharge characteristics, excellent charge/discharge cycle durability and high safety, and an efficient and advantageous process for

5   producing such a lithium cobalt composite oxide, will be provided.

　　Further, a positive electrode for a lithium secondary cell, employing the hexagonal lithium cobalt composite oxide as an active material, and a lithium

10 secondary cell using such a positive electrode, which is excellent in the properties such as the electric capacity, discharge characteristics, charge/discharge cycle durability, capacity density, safety and low temperature operation efficiency, will be provided.

15

CLAIMS

1. A hexagonal lithium-cobalt composite oxide for a
lithium secondary cell, which is represented by the
formula $LiCo_{1-x}M_xO_2$, wherein x is $0 \leqq x \leqq 0.02$ and M is at
5   least one member selected from the group consisting of Ta,
Ti, Nb, Zr and Hf, and which has a half-width of the
diffraction peak for (110) face at $2\theta = 66.5 \pm 1°$, of from
0.070 to 0.180°, as measured by the X-ray diffraction
using CuK_a as a ray source.

10   2. The hexagonal lithium-cobalt composite oxide for a
lithium secondary cell according to Claim 1, wherein x is
$0.0005 \leqq x \leqq 0.02$, and the half-width of the diffraction
peak for (110) face is from 0.100 to 0.165°.

3. The hexagonal lithium-cobalt composite oxide for a
15   lithium secondary cell according to Claim 1, wherein x is
0, and the half-width of the diffraction peak for (110)
face is from 0.080 to 0.100°.

4. The hexagonal lithium-cobalt composite oxide for a
lithium secondary cell according to Claim 1, 2 or 3,
20   wherein the packing press density of the hexagonal
lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm^3.

5. A process for producing the hexagonal lithium-cobalt
composite oxide for a lithium secondary cell as defined
in any one of Claims 1 to 4, which comprises dry blending
25   a cobalt oxyhydroxide powder having an average particle
size of from 1 to 20 μm and a specific surface area of
from 2 to 200 m^2/g, a lithium carbonate powder having an

average particle size of from 1 to 50 μm and a specific

surface area of from 0.1 to 10 m^2/g, and a powder of an

oxide of metal element M having an average particle size

of at most 10 μm and a specific surface area of from 1 to

5   100 m^2/g, and firing the mixture at a temperature of from

850 to 1,000°C in an oxygen-containing atmosphere.

6. The process for producing the hexagonal lithium-

cobalt composite oxide for a lithium secondary cell

according to Claim 5, wherein the mixture is fired for

10   from 4 to 30 hours.

7. A positive electrode for a lithium secondary cell,

which contains the hexagonal lithium-cobalt composite

oxide for a lithium secondary cell as defined in any one

of Claims 1 to 4, as an active material.

15   8. The positive electrode for a lithium secondary cell

according to Claim 7, having a mixture comprising the

active material, an electrically conductive material and

a binder, supported on a current collector.

9. The positive electrode for a lithium secondary cell

20   according to Claim 7 or 8, wherein the current collector

is aluminum or stainless steel.

10. A lithium secondary cell employing a positive

electrode which contains the hexagonal lithium-cobalt

composite oxide for a lithium secondary cell as defined

25   in any one of Claims 1 to 4, as an active material.

11. The lithium secondary cell according to Claim 10,

wherein a cyclic or chain carbonic ester is used as a

solvent for the electrolyte.

ABSTRACT

A composite oxide suitable for an active material of a positive electrode for a lithium secondary cell which can be used in a wide range of voltage, has a large

5   electric capacity and excellent low temperature performance and is excellent in the durability for charge-discharge cycles and highly safe, a process for its production, and a positive electrode and a cell employing it, are presented.

10   The composite oxide is a lithium-cobalt composite oxide which is represented by the formula $LiCo_{1-x}M_xO_2$, (wherein $0 \leqq x \leqq 0.02$ and M is at least one member selected from the group consisting of Ta, Ti, Nb, Zr and Hf), and which has a half-width of the diffraction

15   peak for (110) face at $2\theta = 66.5 \pm 1°$, of from 0.070 to 0.180°, as measured by the X-ray diffraction using CuK_α as a ray source.

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

As a below named inventor, I hereby declare that:

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

My residence, post office address and citizenship are as stated next to my name.

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY CELL EMPLOYING IT, AND LITHIUM SECONDARY CELL

_____

_____

_____

上記発明の明細書は、

the specification of which

☐ 本書に添付されています。

☐ is attached hereto.

☐ ___月___日に提出され、米国出願番号または特許協定条約国際出願番号を_____とし、
（該当する場合）_____に訂正されました。

☒ was filed on October 5, 2000 _____

as United States Application Number or
PCT International Application Number

PCT/JP00/06959 and was amended on

_____ (if applicable).

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

私は、連邦規則法典第37編第1条第56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

8/97

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一ヶ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s)
外国での先行出願

		Priority Claimed 優先権主張	
11-287781	Japan		
(Number) (番号)	(Country) (国名)		
8/October/1999		☒ Yes はい	☐ No いいえ
(Day/Month/Year Filed) (出願年月日)			
11-287785	Japan		
(Number) (番号)	(Country) (国名)		
8/October/1999		☒ Yes はい	☐ No いいえ
(Day/Month/Year Filed) (出願年月日)			
2000-28860	Japan		
7/February/2000		YES	

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.) (出願番号)	(Filing Date) (出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

PCT/JP00/06959	October 5, 2000
(Application No.) (出願番号)	(Filing Date) (出願日)

Pending
(Status: Patented, Pending, Abandoned)
(現況：特許許可済、係属中、放棄済)

(Application No.) (出願番号)	(Filing Date) (出願日)

(Status: Patented, Pending, Abandoned)
(現況：特許許可済、係属中、放棄済)

私は、私自身の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration
（日本語宣言書）

・委任状：私は下記の発明者として，本出願に関する一切の手続き
を米特許商標局に対して遂行する弁理士または代理人として，
下記の者を指名いたします。
・（弁護士，または代理人の指名及び登録番号を明記のこと）

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: (list name and registration number)

022850

書類送付先	Send Correspondence to:

022850

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Japanese Language Declaration
(日本語宣言書)

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第六の共同発明者の氏名		Full name of sixth joint inventor, if any
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郵便の宛先		Post Office Address

（第六またはそれ以降の共同発明者に対しても同様な情報および署名を提供すること。）

(Supply similar information and signature for third and subsequent joint inventors.)

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